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Procedia Engineering 25 (2011) 1137 – 1140

Procedia Engineering

www.elsevier.com/locate/procedia

Proc. Eurosensors XXV, September 4-7, 2011, Athens, Greece

Discrimination and identification of geographical origin virgin olive oil by an e-nose based on MOS sensors and pattern recognition techniques

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Abstract

In the present work, the potential of an electronic nose to differentiate the geographical origin of the Moroccan virgin olive oils based on their volatile profile was investigated. An electronic gas sensor array system composed of 6 metal oxide semiconductor sensors was used to generate a chemical fingerprint (pattern) of the volatile compounds present in olive oils. Multivariate statistical approach showed good discrimination between the classes of the 27-sample of the dataset population. The results of this study provide promising perspectives for the use of a low-cost and rapid system for the verification of geographical origin of the olive oils based on their volatile profile.

Keywords: Virgin olive oil; E-nose; Data analysis; Principal component analysis; Linear discriminant analysis;

1. Introduction

Virgin olive oil (VOO) represents the main source of fats in the countries of mediterranean basin where the olive oil production is concentrated. VOO aroma is characterized by various volatile compounds that include carbonyl compounds, alcohols, esters and hydrocarbons [1]. The interaction of

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doi:10.1016/j.proeng.2011.12.280

volatiles on the sensing element causes changes in electrical resistance of the sensor, and since sensor kinetics is different, the data produced are converted into an odour fingerprint which can be interpreted with the use of appropriate mathematical techniques, such as Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA). The obtained data are comparable in the sense that different samples may be characterized and discriminated based on their volatile production patterns. In the literature there are several reports that demonstrate the potential of electronic nose in food-relevant applications for the classification of vegetable oils [2], quality control of olive oil aroma [3], quality discrimination of fermented table olives [4], and for the verification of geographical origin and authentication of extra virgin olive oils [5]. Top quality VOOs are generally characterized by their particular sensorial attributes, but this is strongly affected by the operative conditions of the VOO mechanical extraction process [6]. In this context, five geographical Moroccan virgin olive oils varieties (OO_Vi with i=1–5) having the same conditions of extraction were used in the experiment. PCA, Radar plot representations and LDA were elaborated to find similarities or differences between the asked geographical VOOs.

2. Experimental

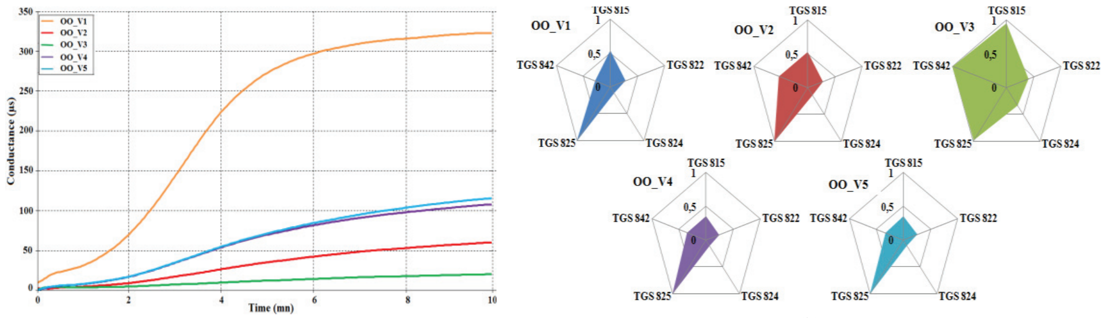
The electronic nose set-up was described in a previous work [7]. The data set has included 27 VOO samples obtained from several olive cultivars and grown in five different regions (Ouarzazate, Ouazzane, Taounate, Mrir't and Sidi Ali). Olives have been harvested in the period from November to December 2010. Once collected, the olives have been extracted in the same conditions and then pressed. Olive oil samples (10 mL) were put in a glass vial and heated at 30 °C for a headspace generation time of 10 min. Then the volatiles were transferred into the sensor chamber by means of a carrier gas (pure nitrogen) at a constant flow-rate for 10 min. The response of the sensors was collected and stored every 2 s. After each measurement, the sensor chamber was opened and cleaned with pure nitrogen gas to generate the sensor baseline. Each time that a new set of VOO was analyzed, new glass vessels were employed.

3. Results and discussion

Fig. 1(a) shows the evolution of the signals generated by TGS 825 sensor. Each line represents the average signal variation of all VOO samples. It can be seen that the sensor signals reach a plateau after a certain time (10 min). However, TGS 821 sensor, with a conductance change near zero, was not used for data analysis. To analyze the response of the e-nose, three meaningful parameters were extracted from each sensor conductance response: the steady-state conductance, the dynamic slope of the conductance and the area below the conductance curve. The features coming from the sensor array measuring in different samples are treated using pattern recognition techniques, such as the Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA) [8].

Extracting the three aforementioned features from each sensor and pre-processing the resulting data matrix were an automated process via a written-in-house MATLAB® program. The LDA (from SPSS software version 17.0) was applied on data set of all features and measurements.

Radar-like plots representation reveals at a glance a clear pattern variation between OO_Vi (with i=1–4). It can be clearly seen, in Fig. 1 (b), that in the fingerprint area, the OO_V4 is close to OO_V5.



(a) (b)

Fig.1. (a) Electrical conductance of TGS 825 sensor towards exposures to VOOs. ; (b) Radar plots for the five VOO varieties.

Fig. 2 reports the three-dimensional score plot in which separation among clusters is almost complete. As one can see, the variances explained by the first three principal components are 77.57 %, 11.88 % and 8.45 %. A clearly obvious discrimination is found between all geographical VOOs. Exception can be made for OO_V4 and OO_V5 which are belonging to Mrir't and Sidi Ali respectively.

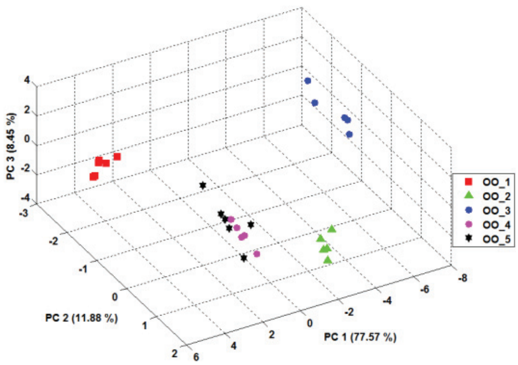


Fig.2. Scores plot of a PCA performed on five VOO measurements gathered using the 5-TGS sensor array.

Applying LDA, a good separation between VOO samples was obtained. Fig. 3 shows how the first two LDA functions discriminate among classes. Function 1 and Function 2 seemed to contribute overall to discriminate mostly between all olive oil varieties.

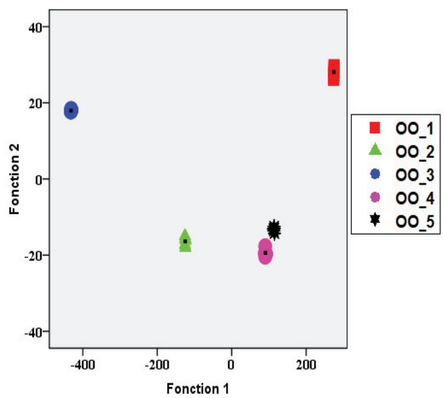


Fig.3. LDA results for the five geographical virgin olive oils discrimination.

LDA model was cross-validated using leave one out approach. An accuracy of 96.3 % success rate in the recognition of the five Moroccan virgin olive oil clusters was achieved (Table 1): only one misclassified sample was detected.

Table 1. Confusion matrix for LDA using leave one out cross-validation approach in the identification of the VOO samples.

Actual	Predicted				
	OO_V1	OO_V2	OO_V3	OO_V4	OO_V5
OO_V1	**6**				
OO_V2		**5**			
OO_V3			**5**		
OO_V4				**5**	
OO_V5				1	**5**

4. Conclusion

This work reports the discrimination and the identification of different VOO samples through electronic nose analysis based on MOS sensors and pattern recognition methods. First of all, PCA analysis was used. The score plot of the PCA exhibited good classification between the different VOO samples with 97.90 % of the variance in the database. An overlap between OO_V4 and OO_V5 was observed. Indeed, Radar plot representations found a clear pattern variation between all geographical VOOs except OO_V4 and OO_V5. Finally, when performing LDA statistical method coupled to leave one out cross-validation of the data, it was possible to deduce a satisfactory accuracy of identification showing more than 96 % of success rate in the recognition of the five Moroccan virgin olive oil clusters.

Acknowledgements

This work has been funded in part by AUF PCSI under project N°: 6313PS025.

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